

## INFLUENCE OF PLANT ASSOCIATIONS ON THE SILICON CYCLE IN THE SOIL-PLANT ECOSYSTEM

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**Abstract.** Soluble Si compounds such as monosilicic and polysilicic acids affect chemicals and physical properties of the soil. The main aim of this study is to evaluate Si cycle in the various soil-plant systems via the determination of mobile Si forms in the soil and of the total content of Si in the plant associations. The concentrations of monosilicic acid, polysilicic acids and acid-extractable Si in unmowed meadow, mowed meadow, birch-aspen forest, spruce wood and agricultural land soil-plant systems, were tested at the soil depths of 0-10, 20-30 and 50-60 cm in a Russian region, south of Moscow. The annual content of Si within the investigated soil-plant systems was calculated. Forty to 80 kg ha<sup>-1</sup> of Si is annually removed from Grey Forest Soil (Luvisol). The concentration of monosilicic acid in the upper soil horizon depended on the type of plant association and on the total content of adsorbed Si. The removal of plant remains from the ecosystems resulted in decreased monosilicic acid concentration in the upper soil horizon. The ecosystems which utilize annual plant remains increased the content of monosilicic acid of the surface soil horizon. The concentration of monosilicic acid in the upper soil layer can be used as indicator of the stability of plant association. The unmowed meadow and the birch-aspen forest were characterized as ecosystems with accumulative type of Si cycle. The agricultural land, the mowed meadow and spruce wood all had alluvial type of Si cycle.

**Keywords:** *monosilicic acid, plant association, polysilicic acid, silicon cycle, soil-plant ecosystem*

### Introduction

Silicon (Si) is the second most abundant element of the earth surface. Numerous chemical, physical and biological soil processes are realized and controlled by this element (Matichenkov and Bocharnikova, 2001; Snyder et al., 2006). The content of Si usually ranges from 20-35% for clay or silt soils to 40-44% for sandy soils (Essington, 2003). Mainly, Si is present as quartz, alkaline earth and aluminum silicates, which forms a soil skeleton and these forms of Si are chemically or biochemically inert, but have influence on the soil physical properties (Conley 2002; Sommer et al., 2006). In the element mobility classification, Si is located in two positions as inert and as mobile element (Matichenkov et al., 2000). Mobile Si substances correspond to monosilicic acid, polysilicic acid, organo-silicon compounds and complex compounds with organic and inorganic substances (Matichenkov and Bocharnikova, 2001). These substances play a primary role in the global biogeochemical cycle of Si (Matichenkov and Bocharnikova, 1994; Wollast and McKenzie, 1983). Plant adsorbs Si in monosilicic acid or their anion forms (Epstein, 1999; Ma, 2003). The removal Si from the soil by plants can range from 20-40 kg/ha for terrestrial ecosystems characterized by low level of biomass increasing up to 3000 kg/ha, which typifies the tropical and subtropical

zones (Anderson, 1991; Wattean and Villemin, 2001). About 27.5 million tons of Si are adsorbed by plants and removed from cultivated areas annually (in comparison to P-absorption, whose annual amount is of 18 million tons) (Bocharnikova and Matichenkov, 1994). Our calculations demonstrate that about 460 million tons of Si is annually involved in the global biological cycle, of which about 341 million tons of Si are in the continental ecosystems (Matichenkov and Bocharnikova, 1994). The intensification and volume of Si cycle in the terrestrial ecosystems can be compared with the cycle of such elements as phosphorus, potassium and calcium (Alexander et al., 1996; Exley, 1998; Lucas et al., 1993). However, the information about the terrestrial Si cycle and the effect of plant association relative to the forms and concentration of Si substances in the soil, are scanty and inadequate in order to better define the role and function of this element in the nature. Besides, to evaluate the biogeochemical Si cycle, only the total content of mobile Si is usually analyzed (Alexander et al., 1996; Bartoli, 1985; Basile-Doelsch et al., 2005; Lucas et al., 1993). Whereas there are at least three forms of mobile Si which are present in the soil (Dietzel 2002; Iler, 1979; Matichenkov and Bocharnikova, 2001). These are: monosilicic acid, polysilicic acid and organo-silicon compounds.

Monosilicic acid is highly biochemical and geochemical active (Iler, 1979; Ma, 2003; Matichenkov et al., 2000). Monosilicic acid can control the mobility of phosphates and can transform plant-unavailable P into plant-available by the replacement of P from Ca, Al and Mg phosphates (Matichenkov and Ammosova, 1996). Al, Mg and heavy metal toxicity may be also suppressed by monosilicic acid (Birchall, 1992; Bocharnikova et al., 1999). Monosilicic acid has an effect on soil pH level (Iler, 1979). It controls the formation of secondary minerals and also the intensity of mineral weathering processes in the soil (Orlov, 1985; Olier, 1990; Horigushi, 1988). Monosilicic acid may be absorbed by plants and microorganisms (Epstein, 1999; Ma, 2003).

Monosilicic acid is a product of Si containing minerals dissolution (Essington 2003; Iler, 1979). The solubility of minerals depends on the chemical structure and size of its particles. The highest solubility is inherent in amorphous silica with high surface area (Iler, 1979). In the surface soil horizons, amorphous silica is represented by biogenic silica forms (plant and microorganism phytoliths) and abiogenic substances formed as a result of precipitation and dehydration of soluble Si compounds (Clarke 2003; Bobrova, 1995; Summer et al., 2006). In plants and soil microorganisms, about 90% of adsorbed monosilicic acid transforms into polymers or biogenic amorphous silica (Alexandre et al., 1996). Biogenic amorphous silica returns to the soil with plants or microbial remains and becomes a new source for monosilicic acid (Sommer et al., 2006). By this means Si cycle is realized via monosilicic acid migration and transformation (Matichenkov and Bocharnikova, 1994). We suggested that monosilicic acid plays a primary role in the terrestrial biogeochemical cycle of Si and provides for the movement of this element in the cycle itself (Matichenkov et al., 2000).

Polysilicic acid has two or more atoms of Si (Iler, 1979; Dietzel, 2002). Some molecules of polysilicic acid have thousands of Si atoms and can represent chains and branch of spherical forms of molecules (Chadwick et al., 1987 a; Chadwick et al., 1987 b). The term of "polysilicic acid" is under discussion now (Iler, 1979; Knight and Kinrade, 2001). It is recognized the following forms of polysilicic acid, as soluble silicic acid, which has more than 2 atoms of Si: oligomers (low molecular weight polysilicic acid), polysilicic acid (high molecular polysilicic acid, but without solid

nucleus) and colloids, which according chemical classification must have solid nucleus and size from  $10^{-7}$  to  $10^{-5}$  cm. Oligomers of silicic acids are characterized by high chemical activity (Dietzel, 2002; Knight and Kinrade, 2001). Our and literature data showed that this substances can be measured together with monosilicic acid, because during 10 minutes of interaction with molybdenum ammonium all monosilicic acid and most part of oligomers are formed colored compels (Dietzel, 2002; Matichenkov, 1990). The colloidal particles of polysilicic acid stir up solution, therefore we suggested to use centrifuge or fine filter for removing of these particles form other form of high molecular weight polysilicic acid (Matichenkov, 1990). It is necessary to recognize truth polysilicic acid and colloidal polysilicic acid because there are has different physical and chemical properties (Yazinin 1989, Matichenkov, 1990). Polysilicic acid has definite effect on soil adsorption capacity and soil structure (Yazinin, 1989; Matichenko et al., 1996). Polysilicic acid is chemically inert and is formed as the result of monosilicic acid polymerization (Iler, 1979; Matichenkov et al., 1996). Other ways of polysilicic acid formation were hypothesized but were not experimentally confirmed, for example, the direct formation from weathered minerals (Nazarov, 1976).

Plant associations and soil interplay and has great influence on each other (Alexandre et al., 1997; Bartoli, 1983; Basile-Doelsch et al., 2005). However the processes of interaction between single plant and plant association on the content and behaviors of Si are investigated poor. The understanding of the biogeochemical cycle of Si processes require more information about behavior of various forms of mobile Si in he soil-plant syetm.

We hypothesized that various plant associations absorb monosilicic acid differentially and may control the concentration of monosilicic acid and polysilicic acid in the upper soil horizons. As a result, a natural or anthropogenic change in plant association can modify Si cycle and influence soil mineral formation, weathering processes and some chemical and physical soil parameters.

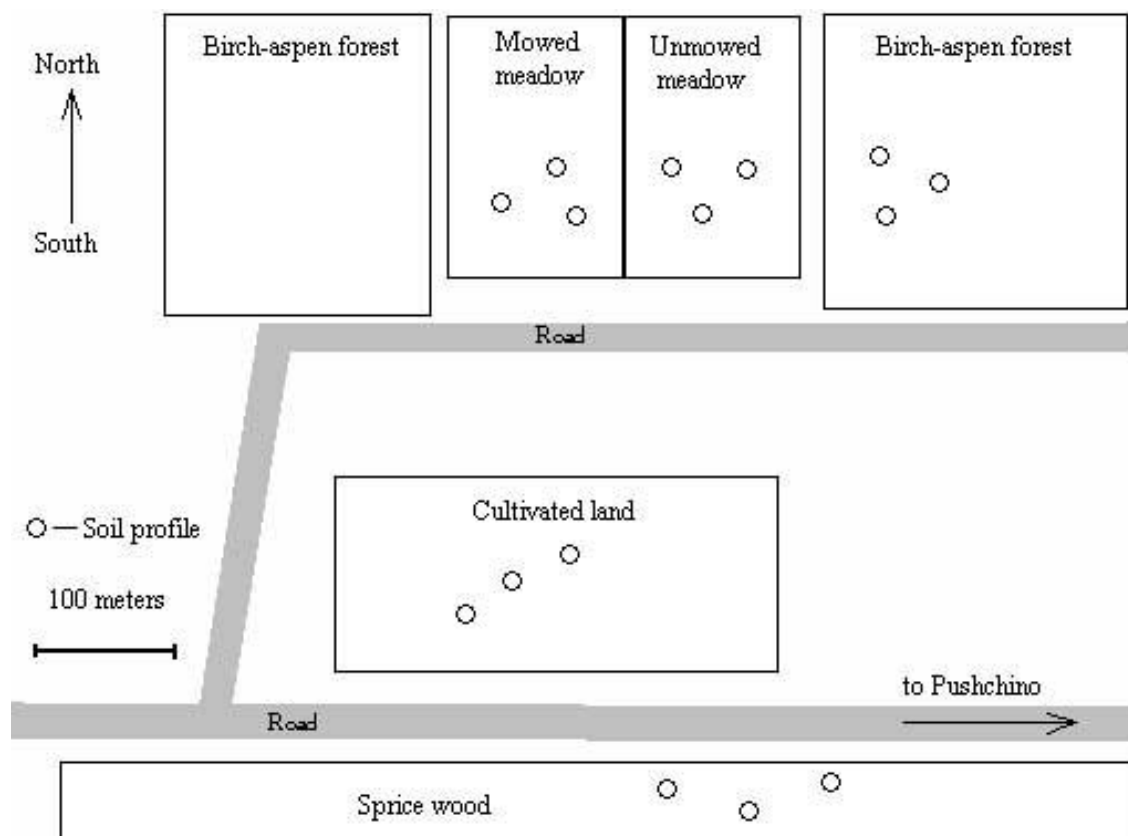
The main aim of this study was to determine soil mobile Si substances in the five soil-plant systems, the total content of Si in plant association for boreal climatic zone and to evaluate the biogeochemical cycle of Si.

## Materials and methods

The selected ecosystems were located on the third terrace of the right side of river-bank of Oka River, south of Moscow region and 5 km west of Pushchino. This area was described as having identical quaternary period sediments, exposition and type of soil (Bazilevich, 1993; Yermolaev and Shirshova, 1994). The scheme of tested area is presented on *Fig.1*.

The unmowed and mowed meadows were used for long-term experiment, conducted by the Institute of Physical-Chemical and Biological Problems in Soil Science (Yermolaev and Shirshova, 1994). Sixteen years ago these areas were separated from plough land, which was used for agriculture over hundred of years. During this experiment, natural evolution of plant associations was examined by supporting meadows under unmowed and mowed technologies. Both plots were located on a slightly ( $3-5^{\circ}$ ) northern slope.

Plant from each plant association was described. The soil profiles for each plant association were prepared in third replication and type of each soil was determined.



**Figure 1.** The scheme of the ecosystems and location of soil profiles

Grass and grass-rich herb phytocenosis were predominant in the meadow vegetation. The main components of the herbage were the following types: loose-tussock, and quitches grasses: *Elytrigia repens* L., Nevski, *Bromopsis inermis* Leyss. Holub., *Dactylis glomerata* L., *Festuca pratensis* Huds., *Pod compressa* L., *Phleum pratense* L., *Anthoxanthum odoratum* L., and *Trifolium hybridum* L., *Trifolium pratense* L.

Various cereals (*Festuca pratensis* Huds., *Phleum pratense* L., and *Pod compressa* L.) were characteristic of the unmowed meadow. *Trifolium pratense* L., *Lathyrus pratensis* L. and other non-cereals were typical of the mowed meadow.

Soil profiles of both meadows were identical. The soil was determined as Typical Grey Forest Soil (Russian Soil Classification) or Luvisol (FAO, 1991). Soil profile has the following description:

Horizon A (0-30 cm) was dark gray, with many average- and small-sized roots, damp clay-sand texture, courses of earthworms, clear boundary, and gradual transition to deeper horizon.

Horizon AB (30-70 cm) was brown with gray stains, small-sized roots, courses of earthworms, and damp clay-sand texture.

The ploughed land with barley (*Hordeum vulgare*) was located near the investigated meadows (200 m to the north-west). The soil was identical to the meadow soil, except the surface horizon (0-30 cm), which was formed by annual tillage. It didn't have roots and its color was more homogeneous. This field has been used in agriculture for over one hundred years (Yermolaev and Shirshova, 1994).

The next plant association was described in the forest. The secondary birch-aspen forest was located beside the mowed and unmowed meadows, on a slight northern slope

(Figure 1). This area had the following plant composition and structure: the lime-birch-aspen wood – hazel, rich in grasses (*Tilia cordata* Mill. + *Betula pendula* Roth + *Populus tremula* L. – *Corulus avellana* L. – *Lonicera Xylosteum* L. Dum - *Pulmonaria obscura* + *Conval baria majlis* L - *Fragaria vesca* L. + *Veronica chamaedris* L.). Plant samples in these points were collected separately for grasses, trees leaves and trees branches. The type of soil was classified as Light Grey Forest. The soil profile had the following structure:

Horizon A (0-12 cm) was gray, moist sand-clay with many large-, average-, and small-sized roots, and gradual transition to deeper horizon.

Horizon A2B (12-30 cm) was light gray with light brown stains, damp sand-clay texture, average and large roots, and gradual transition to deeper horizon.

Horizon AB (30-70 cm) was characterized by heterogeneous mixture of grays, browns and whites and damp sand-clay texture.

The final selected plant association was located in coniferous forest. The spruce wood was located on a hill with a few equal horizontal river platforms (10-15 m) alternated with southern slopes (5-10 m and 20-35°) (Figure 1). It had the following plant composition and structure: *Picea abies* L. Karst + single *Populus tremula* L. without grass cover. Plant samples in these ecosystems were collected separately for needles and for branches of spruce. The type of soil was classified as Grey Forest with the following profile structure:

Organic litter (0-3 cm) represented damp and friable old needles and branches.

Horizon A1 (3-12 cm) was dark gray, with few large roots, damp clay-sand texture, unclear boundary and gradual transition to deeper horizon.

Horizon A2B (12-40 cm) was characterized by heterogeneous light gray color with brown stains, damp clay-sand texture, unclear boundary and gradual transition to deeper horizon.

Horizon AB (40-80 cm) was similar to horizon A2B, brown without light gray material.

Soil and plant samples were pick out from each described ecosystems. Double soil samples were collected from each soil profile at the depth of 0 to 10 cm, 20 to 30 cm and 50-60 cm. The mixed plant samples (total herb cutting from 25 × 25 cm area) were collected from each point of soil sample, with three replications. Plant samples were measured and dried at 65°C. Then plant samples were grounded and then passed through a 0.5-mm sieve. Total Si was tested by Eliot and Snyder (1991) method with four replications for each sample. Samples of plant tissue weighing 100 mg were wetted with 2 mL of 50% H<sub>2</sub>O<sub>2</sub> in 100-mL polyethylene tubes. To each tube was added 4.5 g of 50% NaOH at ambient temperature, and each tube was gently vortexed. The tubes were individually covered with loose-fitting plastic caps. The rack of tubes was placed in an autoclave at 138 kPa for 1 h. After atmospheric pressure was reached, the tubes were removed and the contents brought to 50 mL with distilled water (Eliot and Snyder, 1991). Monosilicic acid in final solution from tubes was determined colorimetrically (Mallen and Raily method cited by Iler, 1979). The average content of total Si was calculated for each point.

Each fresh soil sample was divided into 2 sub-samples. One-half of the sub-samples was air-dried and grounded to pass a 1-mm sieve. These dried soil samples were tested for biogeochemically active amorphous silica (Matichenkov et al., 1997). The remaining sub-samples were maintained under fresh condition after removing roots and passing through a 2-mm sieve. Monosilicic acid was determined in water extracted

from fresh soil samples (Mallen and Raily method cited by Iler, 1979). The extraction procedure was conducted in the following manner: 6 g of fresh soil were placed into beakers. Thirty mL of distilled water were added to each beaker. After 1-hour shaking, the sample was filtered through filter paper No.40, then the extract was analyzed for monosilicic acid. Polysilicic acid was analyzed in the same extract after depolymerization. For depolymerization, an aliquot (20-25 mL) was subjected to ultrasound for 1 min. During this time, all of polysilicic acid was transformed into monosilicic acid (Matichenkov et al., 1997). It should be noted from our earlier work that a change in soil moisture from 50 to 500 g kg<sup>-1</sup> has no effect on the sensitivity of this method (Matichenkov et al. 1997; Matichenkov and Snyder, 1996).

Biochemically active amorphous Si was tested in dry soil samples after a 1day acid extraction procedure (20 mL 0.1 M HCl from air-dried, 2-g sample) (Barsykova and Rochev, 1979). The extract was filtered through filter paper No.40 and analyzed for Si content using the colorimetric method (Mallen and Raily method cited by Iler, 1979). The concentration of Si was determined photo metrically at 660 nm. pH level and moisture of tested soils was determined by standard methods (Thomas,1996).

All obtained data was subjected to a statistical analysis based on comparative methods using Duncan's multiple range tests for mean separation at the 5% level of significance (Duncan, 1955).

The literary data on biomass productivity of tested ecosystems was used for the calculation of Si including the biological cycle (Yermolaev and Shirshova, 1979; Bazilevich, 1993). Only above-ground biomass was used for these calculations.

## Results

The maximum amount of monosilicic acid in the surface horizons was observed for unmowed meadow (17.7 mg Si kg<sup>-1</sup>) and birch-aspen forest (16.2 mg Si kg<sup>-1</sup>) (*Table 1*). Lower concentrations of monosilicic acid in the surface horizons were tested for cultivated soil (6.5 mg Si kg<sup>-1</sup>), the mowed meadow soil (8.6 mg Si kg<sup>-1</sup>) and the spruce wood soil (9.9 mg Si kg<sup>-1</sup>). It is necessary to note that concentrations of monosilicic acid in the soil surface horizons of all investigated ecosystems were significantly different. With depth, the concentration of monosilicic acid tended to increase, ranging from 10.2 to 15.6 mg Si kg<sup>-1</sup>.

The cultivated soil was characterized by the highest concentration of polysilicic acid: 25 mg Si kg<sup>-1</sup>. The soils of both meadows at the depth of 20-30 cm were also characterized by high concentration of polysilicic acid (26.2-30.3 mg Si kg<sup>-1</sup>) (*Table 1*). Both forest soils had the lowest concentration of polysilicic acid, except the subsurface horizon under birch-aspen forest. In the rest soil horizons of the forest ecosystems, the polysilicic acid concentration ranged from 1.8 to 9.6 mg Si kg<sup>-1</sup>.

The difference in amorphous silica concentration in the investigated soils wasn't as high as that in silicic acids (*Table 1*). The maximum concentration of amorphous silica was determined in the deeper horizons. Its value in the lower horizons for forest ecosystem and moved meadow were not significantly different (*Table 1*). The unmowed meadow soil and cultivated soil exhibited the maximum concentration of amorphous silica in the surface soil horizons (527 and 500 mg Si kg<sup>-1</sup>, respectively) (*Table 1*).

**Table 1.** Concentration of soil Si compounds (mg Si kg<sup>-1</sup>)

| Samples                           | pH   | W%   | Monosilicic acid | Polysilicic acid | Acid-extractable Si |
|-----------------------------------|------|------|------------------|------------------|---------------------|
| -----mg Si kg <sup>-1</sup> ----- |      |      |                  |                  |                     |
| <b>Mowed meadow</b>               |      |      |                  |                  |                     |
| 0-10 cm                           | 5.87 | 19.4 | 8.6i             | 18.9d            | 415cd               |
| 20-30 cm                          | 5.66 | 14.6 | 10.8g            | 26.2b            | 455c                |
| 50-60 cm                          | 6.01 | 13.2 | 12.1e            | 7.8h             | 537b                |
| UNMOWED MEADOW                    |      |      |                  |                  |                     |
| 0-10 cm                           | 6.24 | 20.8 | 17.7a            | 15.8e            | 527b                |
| 20-30 cm                          | 6.05 | 14.5 | 10.2gh           | 30.3a            | 468c                |
| 50-60 cm                          | 6.01 | 13.2 | 13.1e            | 7.5h             | 548b                |
| AGRICULTURAL LAND                 |      |      |                  |                  |                     |
| 0-10 cm                           | 6.28 | 13.0 | 6.5j             | 25.0c            | 500bc               |
| 20-30 cm                          | 6.14 | 13.0 | 6.5j             | 25.0c            | 510b                |
| 50-60 cm                          | 6.06 | 17.6 | 13.9d            | 12.7f            | 592a                |
| <b>Birch-aspen forest</b>         |      |      |                  |                  |                     |
| 0-10 cm                           | 6.22 | 13.4 | 16.2b            | 4.1i             | 382d                |
| 20-30 cm                          | 5.12 | 12.3 | 11.5f            | 18.6d            | 428c                |
| 50-60 cm                          | 5.47 | 12.9 | 15.3c            | 1.8j             | 532b                |
| <b>Spruce wood</b>                |      |      |                  |                  |                     |
| 0-10 cm                           | 4.76 | 25.6 | 9.9h             | 8.1h             | 432c                |
| 20-30 cm                          | 5.87 | 13.7 | 14.4d            | 1.8j             | 539b                |
| 50-60 cm                          | 6.16 | 10.8 | 15.6c            | 9.6g             | 534b                |

†Value within a column followed by the same letter are not different using Duncan's Multiple Range test (P<0.05).

The total content of Si in plant association is presented in *Table 2*. The highest concentration of Si (1.75 % from dry mass) was observed in the spruce needles. This data correspond with Bazilevic's content of Si in the needles of *Picea abies*, which was determined in same region (1993). It is necessary to note that content of Si in the spruce needles from mountain region area are lower (Carnelli et al., 2001), which can be explain by difference in the mobile Si content in the soils.

The plant association in the unmowed meadow and barley collected from cultivated area was also characterized by high content of Si in green mass of plants (*Table 2*). This content of Si is typical for cereals (Ma, 2003). Then ext level of total Si in plant association was 1.15% and this level was determined in grass cover of birch-aspen forest. The content of total Si which was determined for plants from mowed meadow and leafs from birch and aspen trees fluctuate around 1.03 - 1.06 % of Si (*Table 2*). The lowest concentrations of Si in plants were determined in the trees branches. It is important to note that the content of Si in the spruce wood was three times higher then in birch or aspen trees (*Table 2*).

The obtained and literature data allowed us to calculate the balance of Si in the tested plant associations (*Table 3*). The calculated data of Si pool in the ecosystem biomass has demonstrated that the maximum Si (87.6 kg Si ha<sup>-1</sup>) was present in the spruce wood biomass (*Table 3*). About half of the plant adsorbed Si was concentrated in the wood. Trees were accumulating this Si during 30-40 years. The annual Si absorption by spruce

was only 40.2 kg Si ha<sup>-1</sup> plus about 2–4 kg Si ha<sup>-1</sup> accumulated in the wood. Consequently, we can suggest that the most active annual Si uptake by plants occurs in the unmowed meadow and agricultural ecosystem (79.1 and 81.5 kg Si ha<sup>-1</sup>, respectively) (Table 3). The lowest Si absorption was calculated for the birch-aspen forest.

**Table 2.** The total content of Si in the tested plant associations

| Area               | Total Si, % from dry mass |
|--------------------|---------------------------|
| Unmowed meadow     | 1.49 <b>b</b>             |
| Mowed meadow       | 1.03 <b>d</b>             |
| Cultivated land    | 1.34 <b>b</b>             |
| Birch-aspen forest |                           |
| grass              | 1.15 <b>c</b>             |
| trees leafs        | 1.06 <b>d</b>             |
| trees branches     | 0.36 <b>e</b>             |
| Spruce wood        |                           |
| needles            | 1.75 <b>a</b>             |
| branches           | 0.97 <b>d</b>             |

†Value within a column followed by the same letter are not different using Duncan's Multiple Range test (P<0.05).

The amount of annually returned biomass into the soil is important in order to calculate Si balance in an ecosystem (Bazilevich,1993). The removal of plant biomass as crops from cultivated land and meadow cutting, is approximated 95% of above-ground vegetable mass. In wood ecosystems, some Si absorbed is found in the wood mass (50% in birch-aspen forest and 54% in spruce woods) (Table 3). Probably all this Si will not return into the soil because local forest district moves out wood material. Only in the unmowed meadow soil-plant system, all of the absorbed Si returns into the soil (Table 3).

**Table 3.** The biological Si cycle in various soil-plant systems

| Area               | Annual increase in biomass t/ha/year | Annual returning plant debris into soil, % | Annual removal of Si from soil, kg Si ha <sup>-1</sup> | Annual return of Si into soil, kg Si ha <sup>-1</sup> | Balance of Si |
|--------------------|--------------------------------------|--------------------------------------------|--------------------------------------------------------|-------------------------------------------------------|---------------|
| Unmowed meadow     | 5.21                                 | 100                                        | 78.09                                                  | 78.09                                                 | 0             |
| Mowed meadow       | 5.98                                 | 5                                          | 61.14                                                  | 3.07                                                  | -58.07        |
| Cultivated land    | 6.10                                 | 5                                          | 81.50                                                  | 4.07                                                  | -77.43        |
| Birch-aspen forest |                                      |                                            |                                                        |                                                       |               |
| green mass         | 2.5                                  | 50                                         | 27.75                                                  | 27.75                                                 | -16.99        |
| wood               | 4.72                                 | 0                                          | 16.99                                                  |                                                       |               |
|                    |                                      |                                            | sum - 44.74                                            |                                                       |               |
| Spruce wood        |                                      |                                            |                                                        |                                                       |               |
| green mass         | 2.3                                  | 46                                         | 40.25                                                  | 40.35*                                                | -47.40*       |
| wood               | 4.99                                 | 0                                          | 47.40                                                  |                                                       |               |
|                    |                                      |                                            | sum - 87.65                                            |                                                       | sum -87.65*   |

\* Needles fallen don't mix with soil forming surface layer (0-3 cm).

## Discussion

Primary and secondary soil minerals are the principal sources of soluble Si forms. Soil Si-rich minerals differ in solubility and are influenced by numerous factors such as pH, particle size, chemical composition, climate, plants, soil microorganisms activity et al. (Lucas et al., 1993). It is possible to distinguish 3 main directions of Si migration and transformation in the soil: leaching of soluble Si-rich compounds without transformation, adsorption of monosilicic acid by plant roots with consequent transformation of monosilicic acid into amorphous silica, and transformation of soluble forms of Si into the soil without movement from the soil profile. The pool of Si leached depends on the amount of atmospheric precipitates and velocity of weathering (Matichenkov et al., 2000). Polysilicic acids are more leachable, than monosilicic acid, and this is due to the peculiar chemical structure of these substances. (Matichenkov et al., 1996). Monosilicic acid has a positive charged anion which is absorbed very well by the soil particles, while the non-compensated electrical charge of polysilicic acid can be self- neutralized by the high flexibility of polysilicic acid molecule (Iler, 1979). Plant roots and soil microorganisms produce organic acids that accelerate mineral weathering (Alexandre, et al., 1996; Drever, 1993).

Higher plants are responsible for the absorption of Si via monosilicic acid through the soil profile. In plant tissues, Si precipitates as phytoliths in cell walls or filling of the cell lumen and in the intercellular spaces (Alexandre et al., 1996). Soil microorganisms adsorb monosilicic acid and then transform it into polysilicic acid and amorphous Si. When plant or soil microorganism die, the adsorbed and transformed Si returns to the soil. The distribution of phytoliths through the soil profile is conditioned by two different mechanisms: translocation into lower horizons and accumulation in upper soil horizon (Bobrova, 1995).

This means that soil minerals, climate conditions, and living organisms are the prime factors that determine Si movement and transformation also known as Si cycle of the soil-plant ecosystem. There are two main Si cycles in nature: cumulative and eluvial (Matichenkov et al. 2000). The accumulative Si cycle is characterized by soils with accumulation of Si substances in the upper soil layer. Ecosystems with accumulative Si cycles, phytolith formation dominates over leaching Si-rich substances. The steppe ecosystems are an example of this type of Si cycle. The content of phytoliths in such soil may range from 6% to 12% of mass in surface horizon (Bobrova, 1995).

The eluvial Si cycle is characteristic of soils having high levels of physical and chemical weathering besides intensive Si leaching, caused by climatic conditions. Plant activity, in these kinds of ecosystems characterized by this type of Si cycle, may be very high but absorbed Si doesn't accumulate in the soil. For example, tropical rain forests often have the eluvial Si cycle where about 90% of biologically active Si of this ecosystem is found in the biomass, not in the soil (Matichenkov and Bocharnikova 1994). Eighty to 90% of total SiO<sub>2</sub> can be removed from the soil profile in humid tropic zones (Kovda, 1985).

In our study, all examined soil-plant systems were located on similar parent material and formed under equal climatic conditions. Only plant associations were different. As a result the role of plant association in these tested ecosystems had critical significance due to the distinction of Si cycles.

It is obvious that monosilicic acid concentration in the soil depends on the type of plants and the amount of vegetative biomass removed from the ecosystem. Returning biomass in unmowed meadow and birch-spruce forest was responsible for increasing

monosilicic acid in the surface horizon of these ecosystems (*Table 1*). It is interesting that a negative Si balance in birch-spruce forest emerged at the depth of 20-30 cm (*Table 1*). This layer was supplied with tree roots.

The increased concentration of monosilicic acid in unmowed meadow soil is the result of the transformation of Si containing minerals into the following mechanism. A parent material was the primary source of monosilicic acid. First plants absorbed Si and formed phytoliths (*Table 2*). Then plant remains, with formed phytoliths, returns into soil. Phytoliths represent fine amorphous silica whose solubility is usually higher than that of most soil minerals (Iler, 1979). This process repeated annually increased, over time, the content of phytoliths in soil and consequently the concentration of monosilicic acid also increased (*Table 1*).

In spruce wood, absorbed silica is accumulated mainly in the needles (*Table 2*). Fallen needles form a compact surface layer and this layer does not mix with the soil. The decomposition of spruce needles is a long-term process (Bazilevich, 1993). In the upper soil horizon of spruce wood, only small amount of monosilicic acids was observed (*Table 1*).

The cultivated soil and mowed meadow soil were characterized by smaller concentration of monosilicic acids in the upper horizons because in both ecosystems absorbed Si is harvested with the crop and doesn't return to the soil (*Tables 1, 2 and 3*). It is important to notice that this situation has a negative effect on plant growth. A deficiency in Si nutrition leads to decreasing cereals viability and resistance to diseases and insect attacks (Datnoff et al., 1997; Snyder et al., 2006). Cereal growth decreases when Si nutrition is very small (Bocharnikova, 1996; Matichenkov, 1990). Probably, this explains why Si deficiency was responsible for a change in plant association on the mowed meadow where wild Si-rich cereals were displaced by other plants (*Lathyrus pratensis* L., *Trifolium pratense* L.) (Yermolaev and Shirshova, 1994).

The increases content of polysilicic acid in plough soil was probably due to mechanical compaction of agricultural equipment. These results correlate very well with our previous data regarding Chermozem soil (Matichenkov et al., 1996). Machine pressure may increase polysilicic acid in the upper soil horizons, however the chemistry of these processes has been poorly investigated.

The soil at the depth of 20-30 cm in both meadow ecosystems contained high amount of polysilicic acid as well (*Table 1*). This is probably caused by the same reason as in arable areas, where the land was used as tillage 16 years ago and polysilicic acid might have been retained (Yermolaev and Shirshova, 1994).

The concentrations of acid-extractable Si were similar in the upper horizons of all tested soils besides the unmowed meadow and plough land (*Table 1*). This increasing of acid-extractable Si can be ascribed to the acceleration of the weathering process in the cultivated soil and to a significant amount of plant phytoliths in the unmowed meadow soil (Bobrova, 1995; Kovda, 1985). Both processes have identical data on chemical testing (Barsukova and Rochin, 1979; Matichenkov et al., 1997; Matichenkov et al., 2000). The monosilicic acid concentration in both ecosystems may serve as an indicator for the direction of mineral transformation processes that are: the accumulation of phytoliths for the unmowed meadow (high level of monosilicic acid) and the acceleration of weathering for the cultivated soil (low level of monosilicic acid).

The correlating coefficients between different Si forms in the soil (*Table 1*) and the balance of elements in the soil-plant systems (*Table 3*) were calculated. A linear dependence of the type  $Y = AX + B$  was used.

Calculations have demonstrated that a high correlation exists between the concentration of monosilicic acid in the soil and the balance of Si in the ecosystem:  $r=0.98$ ,  $p=0.001$ ,  $sd=0.759$ . The relationship between other examined forms of Si in soil and the balance of Si in the ecosystem had no significant level:

$r = 0.0313$ ,  $p = 0.96$ ,  $sd = 10.82$  for sum of soluble Si forms,

$r = -0.75$ ,  $p = 0.26$ ,  $sd = 7.29$  for polysilicic acid, and

$r = 0.100$ ,  $p = 0.87$ ,  $sd = 73$  for acid-extractable Si.

These calculations showed that monosilicic acid concentration in the upper soil horizon strongly depends on the type of plant association when compared with ecosystems having similar type of soil. Monosilicic acid represents the main component in the biogeochemical Si cycle of the soil-plant ecosystem (Matichenkov, Bocharnikova, 1994; Nazarov, 1976). Monosilicic acid also controls many soil properties and has a direct effect on plants and microorganism growth. In turn, plants (type of plant cover) can control the monosilicic acid concentration in the upper soil horizons as well. As a result, we are dealing with a complicated and self-regulating Si biogeochemical cycle in the soil-plant ecosystem.

The unmowed meadow and birch-aspen forest plant associations are responsible for increasing the concentration of monosilicic acid in the upper soil layer which optimizes plant Si nutrition. Silicon-accumulative plants (grasses) have competition priority. Both ecosystems are characterized by accumulative type of Si cycle. The removal of Si as a result of agricultural activity, grazing or accumulation of Si in unavailable forms (spruce wood) can change Si cycle and cause conversion changes for the soil-plant system: degradation of soil minerals, replacement of plant population where non Si accumulative plants have competitive priority. By this means that agriculture land, mowed meadow and spruce wood have typical eluvial Si cycle.

## Conclusion

This investigation clearly shows that the biological cycle of Si is characterized by 40 to 80 kg Si ha<sup>-1</sup> annually removed from Grey Forest Soil. The monosilicic acid concentration in the upper soil horizons strongly depends on the type of plant association. The removal of plant biomass from the ecosystem results in decreasing monosilicic acid concentration in the upper soil horizons. Si movement from lower soil horizons to surface layer can occur via the adsorption of monosilicic acid by plants and by returning phytoliths into the soil. The concentration of monosilicic acid in the upper soil layer may serve as an indicator of straining in the Si biological cycle, stability of existing plant association and direction of the ecosystem evolution. The unmowed meadow and the birch-aspen forest were characterized as ecosystems with accumulative type of Si cycle. The agricultural land, the mowed meadow and spruce wood are all eluvial type Si cycle.

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